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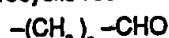
(54) Corrosion inhibition

(57) A method of inhibiting the corrosion of copper or of a metal containing copper, comprising contacting the surface of the copper, or copper containing alloy with a corrosion-inhibiting amount of a mixture of a compound having the formula A:



A

wherein R_1 is C_1-C_{19} straight- or branched chain alkyl, C_5-C_{12} cycloalkyl, C_7-C_{13} aralkyl, optionally substituted C_6-C_{10} or C_{14} aryl, a monocyclic heterocyclic residue having up to 5 ring carbon atoms or a residue of formula I:



I

where $n=1-6$:

and a compound having the formula B



B

where R_2 is C_1-C_{19} straight or branched chain alkyl, C_5-C_{12} cycloalkyl, C_7-C_{13} aralkyl, optionally substituted C_6-C_{10} or C_{14} aryl, a monocyclic heterocyclic residue having up to 5 ring carbon atoms or a residue of the formula II: $-(CH_2)_m-NH_2$ II
where $m=1-6$.

GB 2 204 864

The present invention relates to methods for inhibiting the corrosion of copper; and alloys containing copper; and to compositions in contact with copper and its alloys for inhibiting corrosion.

It is well established that surfaces of copper are susceptible to corrosion, when such surfaces come into contact with aqueous or non-aqueous media. Furthermore, the products of such copper corrosion may catalyse the decomposition of any organic media in contact with the corroding copper surface and may galvanically induce the corrosion of other metals, eg iron or aluminium, which may be present.

Many compounds of widely different structures have been proposed as copper corrosion inhibitors for use in media such as aqueous systems or functional fluids.

Amongst many others, one type of compound which has been found to be effective comprises the Schiff bases derived from the condensation of an aromatic amine and an aromatic aldehyde. In *Surface Coatings and Technology* 27, 175-86 (1986), *N*-(2-mercaptophenyl)salicylideneimine is described as a corrosion inhibitor for copper in aqueous alcoholic media, while in *Surface Coatings and Technology* 29, 141-151 (1986) the same molecule and its analogues are described as corrosion inhibitors for copper and its alloys in acid media.

In earlier publications, Schiff bases have been described as metal corrosion inhibitors in a number of systems. Thus in *J. Electrochem. Soc. India* 32, 397-401 (1983) *N,N'-bis(2-hydroxybenzylidene)ethylenediamine* and *N,N'-bis(4-methoxybenzylidene)ethylenediamine* are described as corrosion inhibitors for zinc in sulphamic acid; in US 3865739 an *N,N'-bis(2-hydroxybenzylidene)ethylenediamine thiadiazole* inhibitor is disclosed; in GB 1434354

the azomethine derived from the condensation of cinnamaldehyde and α -amino-capronitrile is described as an inhibitor for steel in hydrochloric acid.

Against this varied background art, suggesting metal corrosion-inhibition by Schiff bases, we have found, surprisingly, that mixtures of Schiff base precursors provide outstanding copper corrosion inhibition in various media e.g. functional fluids and aqueous systems.

Accordingly, the present invention provides a method of inhibiting the corrosion of copper or of a metal containing copper, comprising contacting the surface of the copper, or copper containing alloy with a corrosion-inhibiting amount of a mixture of a compound having the formula A:



wherein R_1 is C_1-C_{19} straight- or branched chain alkyl, C_5-C_{12} cycloalkyl, C_7-C_{13} aralkyl, optionally substituted C_6 , C_{10} or C_{14} aryl, a monocyclic heterocyclic residue having up to 5 ring carbon atoms or a residue of formula I:



where $n=1-6$:

and a compound having the formula B



where R_2 is C_1-C_{19} straight or branched chain alkyl, C_5-C_{12} cycloalkyl, C_7-C_{13} aralkyl, optionally substituted C_6 , C_{10} or C_{14} aryl, a monocyclic heterocyclic residue having up to 5 ring carbon atoms or a residue of the formula II: $-(CH_2)_mNH_2$

II

where $m=1-6$.

When R_1 or R_2 are C_1-C_{19} alkyl groups, they may be straight- or branched chain eg methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-dodecyl, n-tridecyl, n-pentadecyl, n-heptadecyl or n-nonadecyl.

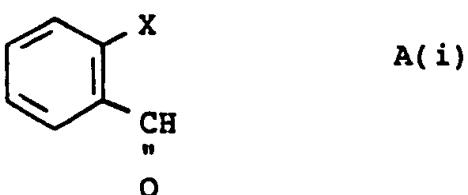
As C_5-C_{12} - cycloalkyl groups R_1 or R_2 may be eg cyclopentyl, cyclohexyl, cyclooctyl, cyclodecyl, adamantyl or cyclododecyl.

As C_7-C_{13} - Aralkyl groups R_1 or R_2 may be benzyl, 2-phenylethyl, benzhydryl or naphthylmethyl.

C_6 , C_{10} or C_{14} Aryl groups R_1 or R_2 are phenyl, naphthyl or anthracenyl. Optional substituents in these aryl groups are eg hydroxyl, thiol, carbonyl, carboxyl or sulphoxyl.

As heterocyclic residues, R_1 and R_2 may be e.g. pyridyl, furfuryl or thiophene.

Preferred compounds of formula A are those having the formula A(i):



where X is hydrogen, hydroxyl, thiol or a group CR_3 where R_3 is hydrogen or hydroxyl.

Other preferred compounds are those of formula A(ii):



where $n=1-6$

Preferred compounds of formula B are those having the formula B(i):



○ where Y is hydrogen, amino, hydroxyl, thiol, carboxyl or sulphoxyl.

Specific example of compounds of formula I for use in the compositions of the compounds include.

Acetaldehyde

Propionaldehyde

Butyraldehyde

Isobutyraldehyde

2-ethylbutyraldehyde

Valeraldehyde

Isovaleraldehyde

Hexanoaldehyde

Heptanaldehyde

Octyl aldehyde

Nonyl aldehyde

Decyl aldehyde

Undecyl aldehyde

Dodecyl aldehyde

Tetradecyl aldehyde

Pentadecyl aldehyde

Hexadecyl aldehyde

Octadecyl aldehyde

Eicosyl aldehyde

Cyclopentanecarboxaldehyde

Cylohexanecarboxaldehyde

Cyclooctanecarboxaldehyde

Cyclododecylcarboxaldehyde

Phenylacetraldehyde

3-phenylpropionaldehyde

Benzhydrol carboxaldehyde

○ Napthylacetaldehyde
Benzaldehyde
Salicaldehyde
3-Hydroxybenzaldehyde
4-Hydroxybenzaldehyde
2-Mercaptobenzaldehyde
3-Mercaptobenzaldehyde
4-Mercaptobenzaldehyde
Phthalaldehyde
Isophthalaldehyde
Terephthalaldehyde
2-Carboxybenzaldehyde
4-Carboxybenzaldehyde
2-sulphobenzaldehyde
4-sulphobenzaldehyde
1-Naphthaldehyde
2-Naphthaldehyde
2-Hydroxy-1-naphthaldehyde
2-Mercapto-1-naphthaldehyde
1-Anthracenaldehyde
2-Anthracenaldehyde
2-Hydroxy-1-anthracenaldehyde
Malonaldehyde
Succinaldehyde
Glutaraldehyde
Adipic aldehyde
1,5-Heptan-dicarboxaldehyde
1,6-Hexan-dicarboxaldehyde
Furfural
Thiophene-2-carboxaldehyde

○ Specific examples of compounds of formula B include

Methylamine

Ethylamine

Propylamine

Isopropylamine

n-Butylamine

sec-Butylamine

tert-Butylamine

n-Amylamine

tert-Amylamine

n-Hexylamine

n-Heptylamine

n-Octylamine

2-Ethyl hexylamine

n-Nonylamine

n-Decylamine

n-Undecylamine

n-dodecylamine

n-Tridecylamine

n-Tetradecylamine

1-Hexadecylamine

1-Octadecylamine

Cyclopentylamine

Cyclohexylamine

Cycloheptylamine

Cyclooctylamine

1-Adamantamine

Cyclodexdecylamine

Benzylamine

2-Phenylethylamine

() Benzhydrylamine

3-Phenylpropylamine

4-Phenylbutylamine

Naphthylmethylamine

Aniline

2-Hydroxyaniline

3-Hydroxyaniline

4-Hydroxyaniline

2-mercaptoaniline

3-mercaptoaniline

4-mercaptoaniline

2-aminobenzaldehyde

Anthranilic acid

3-Aminobenzoic acid

4-Aminobenzoic acid

Sulphanilic acid

2-aminobenzenesulfonic acid

Dimethylamine

1,2-Diethylamine

1,3-Dipropylamine

1,4-Dibutylamine

1,5-Dipentylamine

1,6-Dihexylamine

o-Phenylenediamine

m-Phenylenediamine

p-Phenylenediamine

1-Naphthylamine

1-Amino-2-naphthol

1-Amino-7-naphthol

3-Amino-2-naphthol

4-Amino-1-naphthol
8-Amino-2-naphthol
3-Amino-2-napthoic acid
2-Amino-1-naphthalenesulphonic acid
4-Amino-1-naphthalenesulphonic acid
5-Amino-2-naphthalenesulphonic acid
8-Amino-2-naphthalenesulphonic acid
3-Amino-2,7-naphthalenesulphonic acid
7-Amino-1,3-naphthalenedisulphonic acid
1-Aminoanthracene
2-Aminoanthracene
2-Aminopyridine
3-Aminopyridine

The method of treating the metal surface may be by a variety of techniques. For example, the copper surface may be wrapped in a film impregnated with suitable amounts of the compounds of formula A and B, or the copper surface may be dipped into a solution eg an aqueous solution containing suitable amounts of compounds of formula A and B. More usually, however, the metal surface will be permanently in contact with a substrate which causes corrosion of the metal surface. In such cases the surfaces of copper-containing metals can be effectively inhibited against corrosion by adding a corrosion-inhibiting amount of a mixture of compounds of formulae A and B. The mixture in all the above methods may contain non-equimolar amounts of A and B, e.g. in a ratio of from 3:1 to 1:3, but preferably contains an equimolar composition.

The present invention, therefore, also provides a composition comprising a substrate in contact with copper, or a

preferably 0.001% to 5% by weight, more preferably 0.01% to 1% based on total weight of the substrate, of a composition of compounds of formulae A and B as hereinbefore defined.

Examples of substrates which may be treated according to the present invention include functional fluids such as lubricants eg those having a mineral oil, poly-alpha olefin or synthetic carboxylic acid ester base; hydraulic fluids eg those based on mineral oils, phosphate esters, aqueous polyglycol/polyglycol ether mixtures or glycol systems; oil-in-water or water-in-oil systems; metal-working fluids having, as their base, mineral oil or aqueous systems; water- or aqueous glycol- or ethylene- or propylene glycol/methanol based engine coolant systems; transformer- or switch oils; as well as aqueous systems eg industrial cooling water; aqueous air-conditioning systems; steam-generating systems; sea-water evaporator systems; hydrostatic cookers; and aqueous closed circuit heating or refrigerant systems.

When a functional fluid substrate is a synthetic lubricant, examples thereof include lubricants based on a diester of a dibasic acid and a monohydric alcohol, for instance dioctyl sebacate or dinonyladipate; on a triester of trimethylolpropane and a monobasic acid or mixture of such acids, for instance trimethylol propane tripelargonate, trimethylolpropane tricaprylate or mixtures thereof; on a tetraester of pentaerythritol and a monobasic acid or mixture of such acids, for instance pentaerythritol tetracaprylate; or on complex esters derived from monobasic acids, dibasic acids and polyhydric alcohols, for instance a complex ester derived from trimethylol propane, caprylic acid and sebacic acid; or of mixtures thereof.

Other synthetic lubricants are those known to the art-skilled and described eg in "Schmiermittel-Taschenbuch" (Huethig Verlag, Heidelberg 1974). Especially suitable, apart from the preferred mineral oils are eg phosphates, glycols, polyglycols, polyalkylene glycols and poly-alpha olefins.

In order to improve various applicational properties, a functional fluid composition of the invention may also contain other additives such as, for oil-based systems, one or more of antioxidants, metal deactivators, further corrosion or rust inhibitors, viscosity-index improvers, pour-point depressants, dispersants/surfactants and/or anti-wear additives; and for aqueous-based systems, one or more of antioxidants, other corrosion- and rust inhibitors, metal deactivators, extreme pressure- or anti-wear additives, complexing agents, precipitation inhibitors, biocides, buffering agents and/or anti-foams.

For oil-based systems, examples of other additives are:

Examples of phenolic antioxidants

1. Alkylated Monophenols

2,6-Di-tert.-butylphenol

2-tert.-butyl-4,6-dimethylphenol

2,6-Di-tert.-butyl-4-ethylphenol

2,6-Di-tert.-butyl-4-n-butylphenol

2,6-Di-tert.-butyl-4-i-butylphenol

2,6-Di-cyclopentyl-4-methylphenol

2-(β -Methylcyclohexyl)-4,6-dimethylphenol

2,6-Di-octadecyl-4-methylphenol

2,4,6-Tri-cyclohexylphenol

2,6-Di-tert.-butyl-4-methoxymethylphenol

2. Alkylated Hydroquinones

2,6-Di-tert.-butyl-4-methoxyphenol

○

2,5-Di-tert.-butyl-hydroquinone

2,5-Di-tert.-amyl-hydroquinone

2,6-diphenyl-4-octadecyloxyphenol

3. Hydroxylated Thiodiphenylethers

2,2'-Thio-bis-(6-tert.butyl-4-methylphenol)

2,2'-Thio-bis-(4-octylphenol)

4,4'-Thio-bis-(6-tert.butyl-3-methylphenol)

4,4'-Thio-bis-(6-tert.butyl-2-methylphenol)

4. Alkylidene-Bisphenols

2,2'-Methylene-bis-(6-tert.-butyl-4-methylphenol)

2,2'-Methylene-bis-(6-tert.-butyl-4-ethylphenol)

2,2'-Methylene-bis-(4-methyl-6-(α -methylcyclohexyl)-phenol)

2,2'-Methylene-bis-(4-methyl-6-cyclohexylphenol)

2,2'-Methylene-bis-(6-nonyl-4-methylphenol)

2,2'-Methylene-bis-(4,6-di-tert.-butylphenol)

2,2'-Ethylidene-bis-(4,6-di-tert.-butylphenol)

2,2'-Ethylidene-bis-(6-tert.-butyl-4-isobutylphenol)

2,2'-Methylene-bis-(6-(α -methylbenzyl-4-nonylphenol)

2,2'-Methylene-bis-(6-(α , α -dimethylbenzyl)-4-nonylphenol)

4,4'-Methylene-bis-(6-tert.-butyl-2-methylphenol)

1,1'-Bis-(5-tert.-butyl-4-hydroxy-2-methylphenol)-butane

2,6'-Di-(3-tert.butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol

1,1,3-Tris-(5-tert.butyl-4-hydroxy-2-methylphenyl)-3-n-dodecyl-
mercaptobutane

Ethyleneglycol-bis-[3,3-bis-(3'tert.-butyl-4'-hydroxyphenyl)-
butyrate]

Di-(3-tert.-butyl-4-hydroxy-5-methylphenyl)-dicyclopentadiene

Di-[3'-tert.-butyl-2'-hydroxy-5'-methyl-benzyl)-6-tert.-butyl-
4-methyl-phenyl]-terephthalate

5. Benzyl Compounds

1,3,5-Tri-(3,5-di-tert.-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene

Di-(3,5-di-tert.-butyl-4-hydroxybenzyl)-sulfide

Bis-(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)dithiol-terephthalate

1,3,5-Tris-(3,5-di-tert.-butyl-4-hydroxybenzyl)-isocyanurate

1,3,5-Tris-(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)-isocyanurate

3,5-Di-tert.-butyl-4-hydroxybenzyl-phosphonic acid-dioctadecyl-ester

3,5-Di-tert.-butyl-4-hydroxybenzyl-phosphonic acid-monoethylester Calcium-salt

6. Acylaminophenols

4-Hydroxy-lauric acid anilide

4-Hydroxy-stearic acid anilide

2,4-Bis-octylmercapto-6-(3,5-di-tert.-butyl-4-hydroxyanilino)-s-triazine

N-(3,5-di-tert.-butyl-4-hydroxyphenyl)-carbamic acid octyl ester

7. Esters of β -(3,5-Di-tert.-butyl-4-hydroxyphenol)-propionic acid

with mono- or polyhydric alcohols eg with

Methanol Diethyleneglycol

Octadecanol Triethyleneglycol

1,6-Hexandiol Pentaerythritol

Neopentylglycol Tris-hydroxyethyl-isocyanurate

Thiodiethyleneglycol Di-hydroxyethyl-oxalic acid diamide

8. Esters of β -(5-tert.-butyl-4-hydroxy-3-methylphenyl)-propionic acid

with mono- or polyhydric alcohols eg with

Methanol	Diethyleneglycol
Octadecanol	Triethyleneglycol
1,6-Hexandiol	Pentaerythritol
Neopentylglycol	Tris-hydroxyethyl-isocyanurate
Thiodiethyleneglycol	Di-hydroxyethyl-oxalic acid diamide

9. Amides of β -(3,5-Di-tert.-butyl-4-hydroxyphenyl)-propionic acid eg

N,N'-Di-(3,5-di-tert.-butyl-4-hydroxyphenylpropionyl)-hexamethylene-diamine

N,N'-Di-(3,5-di-tert.-butyl-4-hydroxyphenylpropionyl)-trimethylene-diamine

N,N'-Di-(3,5-di-tert.-butyl-4-hydroxyphenylpropionyl)-hydrazine

Examples of amine antioxidants:

N,N'-Di-isopropyl-p-phenylenediamine

N,N'-Di-sec.-butyl-p-phenylenediamine

N,N'-Bis(1,4-dimethyl-pentyl)-p-phenylenediamine

N,N'-Bis(1-ethyl-3-methyl-pentyl)-p-phenylenediamine

N,N'-Bis(1-methyl-heptyl)-p-phenylenediamine

N,N'-Bis(1-methyl-heptyl)-p-phenylenediamine

N,N'-Dicyclohexyl-p-phenylenediamine

N,N'-Diphenyl-p-phenylenediamine

N,N'-Di-(naphthyl-2-)-p-phenylenediamine

N-Isopropyl-N'-phenyl-p-phenylenediamine

N-(1,3-dimethyl-butyl)-N'-phenyl-p-phenylenediamine

N-(1-Methyl-heptyl)-N'-phenyl-p-phenylenediamine

N-Cyclohexyl-N'-phenyl-p-phenylenediamine

4-(p-Toluene-sulfonamido)-diphenylamine

N,N'-dimethyl-N,N'-di-sec.-butyl-p-phenylenediamine

Diphenylamine

N-Phenyl-1-naphthylamine

N-Phenyl-2-naphthylamine

Octylated Diphenylamine

Octylated N-phenyl- (or) naphthylamine

4-n-Butylaminophenol

4-Butyrylamino-phenol

4-Nonanoylamino-phenol

4-Isodecanoylamino-phenol

4-Octadecanoylamino-phenol

Di-(4-methoxy-phenyl)-amine

2,6-Di-tert.-butyl-4-dimethylamino-methyl-phenol

2,4'-diamino-diphenylmethane

4,4'-Diamino-diphenylmethane

N,N,N',N'-Tetramethyl-4,4'-diamino-diphenylmethane

1,2-Di-(phenylamino)-ethane

1,2-Di-[(2-methyl-phenyl)-amino]-ethane

1,3-Di-(phenylamino)-propane

(o-tolyl)-biguanide

Di-[4-(1',3'-dimethyl-butyl)-phenyl]amine

Examples of further metal passivators are:

for copper eg

Benzotriazole, tolutriazole and derivatives thereof, tetrahydrobenzotriazole, 2-mercaptopenzthiazole, 2,5-dimercapto-thiadiazole, salicylidene-propylenediamine and salts of salicylaminoguanidine.

Examples of rust inhibitors are:

a) Organic acids, their esters, metal salts and anhydrides eg N-oleoyl-sarcosine, sorbitan-mono-oleate, lead-naphthenate, dodecenyl-succinic acid (and its partial esters and amides),

○ b) nitrogen-containing compounds eg

I. Primary, secondary or tertiary aliphatic or cycloaliphatic amines and amine-salts of organic and inorganic acids eg oil-soluble alkylammonium carboxylates

II. Heterocyclic compounds eg substituted imidazolines and oxalines

c) Phosphorus-containing compounds eg Amine salts of phosphonic acid partial esters, zinc dialkyldithiophosphates

d) Sulfur-containing compounds eg Barium-dinonylnaphthalene-n-sulfonates, calcium petroleum sulfonates

Examples of viscosity-index improvers are eg

Polymethacrylates, vinylpyrrolidone/methacrylate-copolymers, polybutenes, olefin-copolymers styrene/acrylate-copolymers.

Examples of pour-point depressants are eg

Polymethacrylates, or alkylated naphthalene derivatives

Examples of dispersants/surfactants are eg

Polybutenylsuccinic acid-amides, polybutenylphosphonic acid derivatives, basic magnesium-, calcium-, and bariumsulfonates and -phenolates.

Examples of anti-wear additives are eg

Sulfur- and/or phosphorus- and/or halogen-containing compounds eg sulfurised vegetable oils, zinc dialkyldithiophosphates, tritolyl-phosphate, chlorinated paraffins, alkyl- and aryldisulfides.

In the treatment of substrates which are completely aqueous, such as cooling water systems, air-conditioning system, steam-generating systems, sea-water evaporator systems, hydrostatic cookers, and closed circuit heating or refrigerant systems, further corrosion inhibitors may be used such as, for

example, water soluble zinc salts; phosphates; polyphosphates; phosphonic acids and their salts, for example, hydroxy ethylidene diphosphonic acid, nitrilotris methylene phosphonic acid and methylamino dimethylene phosphonocarboxylic acids and their salts, for example, those described in German Offenlegungsschrift 2632774, hydroxyphosphonoacetic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid and those disclosed in GB 1572406; nitrates, for example sodium nitrate; nitrites eg sodium nitrite; molybdates eg sodium molybdate; tungstates; silicates eg sodium silicate; benzotriazole, bis-benzotriazole or copper deactivating benzotriazole or tolutriazole derivatives or their Mannich base derivatives; N-acyl sarcosines; N-acylimino diacetic acids; ethanolamines; fatty amines; and polycarboxylic acids, for example, polymaleic acid and polyacrylic acid, as well as their respective alkali metal salts, copolymers of maleic anhydride, eg copolymers of maleic anhydride and sulfonated styrene, copolymers of acrylic acid eg copolymers of acrylic acid and hydroxyalkylated acrylic acid, and substituted derivatives of polymaleic and polyacrylic acids and their copolymers. Moreover, in such completely aqueous systems, the triazole copper corrosion inhibitor used according to the invention may be used in conjunction with dispersing and/or threshold agents eg polymerised acrylic acid (or its salts), phosphino-polycarboxylic acids (as described and claimed in British Patent 1458235), the cotelomeric compounds described in European Patent Application No. 0150706, hydrolysed polyacrylonitrile, polymerised methacrylic acid and its salts, polyacrylamide and co-polymers thereof from acrylic and methacrylic acids, lignin sulphonic acid and its salts, tannin, naphthalene sulphonic acid/formaldehyde condensation products starch and its derivatives, cellulose.

C. acrylic acid/lower alkyl hydroxyacrylate copolymers eg those described in US Patent Specification No. 4029577, styrene/maleic anhydride copolymers and sulfonated styrene homopolymers eg those described in US Patent Specification No. 4374733 and combinations thereof. Specific threshold agents, such as for example, 2-phosphonobutane-1,2,4-tri-carboxylic acid, acetodiphosphonic acid, hydrolysed polymaleic anhydride and its salts, alkyl phosphonic acid, hydroxyphosphonoacetic acid 1-aminoalkyl-1, 1-diphosphonic acids and their salts, and alkali metal poly-phosphates, may also be used.

Precipitating agents such as alkali metal orthophosphates, carbonates; oxygen scavengers such as alkali metal sulphites and hydrazines; sequestering agents such as nitrilotriacetic acid and its salts; antifoaming agents such as silicones eg poly-dimethylsiloxanes, distearylsebacamides, distearyl adipamide and related products derived from ethylene oxide and/or propylene oxide condensations, in addition to fatty alcohols, such as capryl alcohols and their ethylene oxide condensates; and biocides eg amines, quaternary ammonium compounds, chlorophenols, sulphur-containing compounds such as sulphones, methylene bis thiocyanates and carbamates, isothiazolones, brominated propionamides, triazines, phosphonium compounds, chlorine and chlorine-release agents and organometallic compounds such as tributyl tin oxide, may be used.

The compounds of formulae A and B combine excellent copper deactivation properties with good solubility in aqueous- and oil-based substrates.

The following Examples further illustrate the present invention. All parts and percentages given therein are by weight.

Examples 1 to 11

A 0.05% solution of an equimolar mixture of components of formulae A and B is produced in 75:25 water:ethylene glycol mixture, in which the water contains $0.132 \text{ g l}^{-1} \text{ MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $0.68 \text{ g l}^{-1} \text{ CaCl}_2 \cdot 6\text{H}_2\text{O}$ (water as used in DIN 51360 test). The pH of the solution is adjusted to 8.5 with sodium hydroxide.

A piece of copper foil ($20 \times 50 \times 0.1 \text{ mm}$) is cleaned by rubbing with cotton wool soaked with water and powdered pumice, dried and weighed. It is then fully immersed in 50 ml of the solution so prepared in a 60 ml bottle fitted with a screw cap. The bottle is then placed for 24 hours in an oven maintained at 70°C . At the end of this time, the strip is removed, washed and dried and its colour is recorded (using the ASTM D130 colour ranking). It is then immersed for 15 seconds in 5N hydrochloric acid at 20°C , washed, dried and reweighed.

The results are summarised in Table I:

Example	Compound of Formula A R ₁	Compound of Formula B R ₂	% inhibition	Test Results Metal Appearance and Rating
	C O N T R O L			
1	2-HO.C ₆ H ₄	2-HO.C ₆ H ₄	0	4D
2	2-HOC ₆ H ₄	2-HS.C ₆ H ₄	41.9	Heavy green film
3	"	2-NH.C ₆ H ₄	67.7	Heavy brown film
4	"	2-CO ₂ H.C ₆ H ₄	83.9	1B
5	C ₆ H ₅	2-HO.C ₆ H ₄	71.0	1B
6	"	2-HS.C ₆ H ₄	69.4	1A/1B
7	"	2-NH ₂ .C ₆ H ₄	95.2	1A/1B
8	"	2-CO ₂ H.C ₆ H ₄	64.5	2C
9	(CH ₂) ₃ CHO	2-CO ₂ H.C ₆ H ₄	100	1A
10	"	4-CO ₂ H.C ₆ H ₄	95.2	Heavy brown film
11	"	4-SO ₃ H.C ₆ H ₄	82.2	3A
			71.0	Black and orange areas

Claims

1. A method of inhibiting the corrosion of copper or of a metal containing copper, comprising contacting the surface of the copper, or copper containing alloy with a corrosion-inhibiting amount of a mixture of a compound having the formula A:



wherein R_1 is C_1-C_{19} straight- or branched chain alkyl, C_5-C_{12} cycloalkyl, C_7-C_{13} aralkyl, optionally substituted C_6 , C_{10} or C_{14} aryl, a monocyclic heterocyclic residue having up to 5 ring carbon atoms or a residue of formula I:



where $n=1-6$:

and a compound having the formula B

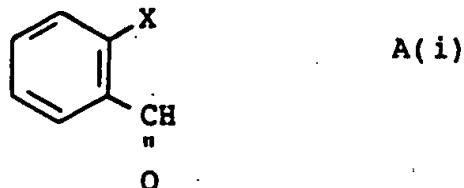


where R_2 is C_1-C_{19} straight or branched chain alkyl, C_5-C_{12} cycloalkyl, C_7-C_{13} aralkyl, optionally substituted C_6 , C_{10} or C_{14} aryl, a monocyclic heterocyclic residue having up to 5 ring carbon atoms or a residue of the formula II:



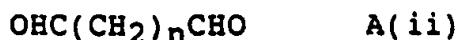
where $m=1-6$.

2. A method as claimed in claim 1 in which the compound of formula A is one of the formula A(i)



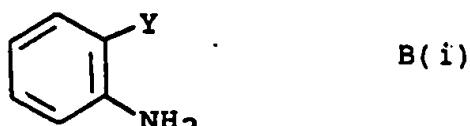
where X is hydrogen, hydroxyl, thiol or a group CR_3 where R_3 is hydrogen or hydroxyl.

3. A method as claimed in claim 1 in which the compound of formula A is one of the formula A(ii)



where n is 1 to 6.

4. A method as claimed in any preceding claim in which the compound of formula B is one of formula B(i)



where Y is hydrogen, amino, hydroxyl, thiol, carboxyl or sulphoxyl.

5. A method as claimed in any preceding claim in which the mixture contains A and B in a molar ratio of from 3:1 to 1:3.

6. A method as claimed in any preceding claim in which the mixture contains equimolar amounts of the compounds A and B.

7. A composition comprising a substrate in contact with copper, or a metal containing copper and a copper corrosion-inhibiting amount of a composition of compounds of formulae A and B as defined.

8. A composition as claimed in claim 7 which contains from 0.001% to 5% by weight, based on the total weight of the substrate, of the composition of compounds of formulae A and B.

9. A composition as claimed in claim 8 which contains 0.01% to 1% of said composition of compounds of formulae A and B.

10. A composition as claimed in claim 9 which contains equimolar amounts of the compounds of formulae A and B.

11. A composition as claimed in any of claims 7 to 10 in which the substrate is a lubricant, a hydraulic fluid, an oil-in-water or water-in-oil system, a metal-working fluid, an engine coolant, a transformer or switch oil, an industrial cooling water, an

aqueous air-conditioning system, a steam generating system, a sea-water evaporator system, a hydrostatic cooker or an aqueous closed circuit heating or refrigerant system.

12. A composition as claimed in claim 11 which is oil-based and also contains an antioxidant, metal deactivator corrosion or rust inhibitor, viscosity index improver, pour-point depressant, dispersant, surfactant and/or anti-wear additive.

13. A composition as claimed in claim 11 which is aqueous based and also contains an antioxidant, corrosion or rust inhibitor, metal deactivator, extreme-pressure or anti-wear additive, complexing agent, precipitation inhibitor, biocide, buffering agent and/or anti-foam agent.

14. A method as claimed in claim 1 substantially as hereinbefore described with reference to any one of the foregoing Examples.

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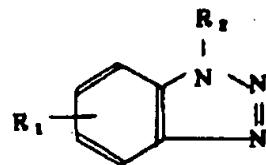
$\text{CH}_3(\text{CH}_2)_n\text{CON}(\text{CH}_3)\text{CH}_2\text{COOH}$

APPLICANT : DAIWA KASEI KENKYUSHO:KK;

INVENTOR : FUJIBAYASHI HIROYUKI;

INT.CL. : C23F 11/14

TITLE : CORROSION INHIBITOR



I

II

ABSTRACT : PURPOSE: To obtain a corrosion inhibitor which is harmless to man and beast and has an improved corrosion inhibiting effect by adding amine to a mixture of specified acylsarcosine with specified benzotriazole.

CONSTITUTION: Amine is added to a mixture of acylsarcosine represented by formula I (where n is an integer of 4~22) with benzotriazole represented by formula II (where R₁ is H, halogen, lower alkyl, hydroxyl or carboxyl; and R₂ is H or 7~17C acyl). The resulting corrosion inhibitor maintains its corrosion inhibiting performance to various kinds of metals over a long term, and it is harmless to man and beast.

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⑭ 防錆剤

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 ⑯ 出 願 昭57(1982)1月29日
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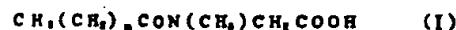
㉑ 代理人 弁理士 倉内基弘 外1名

明 論 審

1 発明の名称 防錆剤

2 特許請求の範囲

(1) 次式(I)



(ここでnは4~22の整数である)

で表わされるアシルザルコシンと次式(II)



(ここでR₁は水素原子、ハロゲン原子、低級アルキル基、ヒドロキシル基又はカルボキシル基を表わし、R₂は水素原子又はC₁~C₁₁アルキル基を表わす)

で表わされるベンゾトリアゾールとの混合物にアミンを付加させて得られるアミン付加塩を含むことを特徴とする防錆剤。

④ アシルザルコシンがカブロイルザルコシン、ペルミトイルザルコシン、ラウロイルザルコシン、ココイルザルコシン、オレオイルザルコシン又はステアロイルザルコシンであることを特徴とする特許請求の範囲第1項記載の防錆剤。

⑤ ベンゾトリアゾールがベンゾトリアゾール、低級アルキルベンゾトリアゾール又はN-アシルベンゾトリアゾールであることを特徴とする特許請求の範囲第1項記載の防錆剤。

⑥ アミンがアルキル若しくはシクロアルキルアミン、アルカノールアミン又は環状アミンであることを特徴とする特許請求の範囲第1項記載の防錆剤。

⑦ アミンがシクロヘキシルアミン、モノエタノールアミン、ジエタノールアミン、トリエタノールアミン、モルホリン、ビペラジン又はビペリジンであることを特徴とする特許請求の範囲第4項記載の防錆剤。

⑧ 5.5~8.5質量%のアシルザルコシンと4.5~1.5質量%のベンゾトリアゾールとの混合物

100重量部にアミン45~80重量部を付加させてアミン付加塗を形成させたことを特徴とする特許請求の範囲第1~5項のいずれかに記載の防錆剤。

(7) 401~5質量%の濃度まで希釈されて使用されることを特徴とする特許請求の範囲第1~6項のいずれかに記載の防錆剤。

3.発明の詳細な説明

本発明は、改善された防錆効果を有する金属防錆剤に関するもの。

本田特許第5791803号には各種のN-アシルベンゾトリアゾールが金属防食剤として有効であることが記載されている。また、特開昭51-13338号、本田特許第5791237号及び同4014694号にはベンゾトリアゾールがカルボン酸との併用において鉄及び非鉄金属用の防錆剤として有効であることが記載されている。しかしながら、これらの防食又は防錆剤はいずれも油溶性のものである。さらには、特開昭

特開昭58-130284(2) 2428512号、特公昭50-13750号、同13751号、同13752号及び同13753号にはベンゾトリアゾールがある種のカルボン酸のアミン塩との共存下で防錆に有効であることが記載されている。しかし、これらの防錆剤も同様に油溶性の防錆剤である。

他方、アシルデルコシンはN-メチルグリシンのアシル誘導体であつて、その長鎖アシル誘導体は優れた界面活性剤として広く用いられている。また、これらがそのまま或いはアルカリ又はアミン塩の形で金属の防食剤として有効であることも知られている。

しかし、上述のような防錆又は防食剤の多くは油溶性であること、また鉄鋼用防錆剤は非鉄金属に対してはあまり有効でなく、逆に非鉄金属用は鉄に対して有効でないこと等の欠点を有している。さらに、従来の防錆剤はその防錆効果の落液中に浸漬中の防錆効果は優れているが、落液から引き上げた後は短時間で錆を発生し、さらには処理金属における底色の変化が大きいという欠点を有して

いる。

また、最近の内燃機関における冷却系統には、多種類の金属、例えばアルミニウム、アルミニウム鉄物、鉄、鋼、黄銅、銅、ハンド等が適宜併用されるようになり、このような多種類の金属に対して従来の防錆剤はその適用金属の種類の点で極めて限定されており、有効なものが少なかつた。このような状況において、多種類の金属を防食するためには多種類の防錆剤を配合して用いているのが実情である。例えば、アルカノールアミンを添加した防錆剤に亜硝酸ナトリウムが配合されて用いられているが、堿基性を有するとみられるエトロソアミンが生成するといわれており、したがつてこれらのアルカノールアミンと亜硝酸ナトリウムとを防錆剤に配合することは便宜にならざるを得ない。

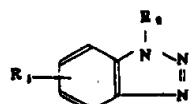
したがつて、本発明の目的は、上述のような従来の防錆剤の欠点を除去することにより、種の金属に対して長期間にわたる充分な防食性を有し且つ水性希釈に適すると共に、人畜に対する安

全性が低い防錆剤を提供することである。

ここに、アシルデルコシンとベンゾトリアゾールとの混合物にアミンを付加させて得られるアミン付加塗を含む防錆剤がベンゾトリアゾール単独又はデルコシン単独の場合よりも金属表面への吸着力及び被覆率を増大させ、防錆効果を相乗的に向上させることが見出された。また、このようにアミン付加塗とすることにより油溶性であるアシルデルコシン及びベンゾトリアゾールを水溶性とすることによって、用途の範囲が広がり、鉄及び非鉄を問わず、多くの金属、例えば鉄、鉄鉄、鋼、黄銅、亜鉛、アルミニウム、ハンド等に対して優れた防食効果を示すことがわかつた。さらに、金属表面に防錆成分の強固なキレート皮膜が形成されることから、防錆効果後から金属を引き上げた後の防錆効果が極めて優れていることがわかつた。また、このようなアミン付加塗は水性用途に固らず、大層の油溶性防錆剤にも共存可能であつて、その防錆効果も一層改善されることもわかつた。

したがつて、マニ

$\text{CH}_2(\text{CH}_2)_n\text{CON}(\text{CH}_2)\text{CH}_2\text{COOH}$
 (ここで n は 4 ～ 22 の整数である)
 で表わされるアシルザルコシンと次式



(ここで R_1 は水素原子、ハロゲン原子、低級アルキル基、ヒドロキシル基又はカルボキシル基を表わし、 R_2 は水素原子又は C_1 ～ C_{11} アシル基を表わす)

で表わされるベンゾトリアゾールとの混合物にアミンを付加させて得られるアミン付加塩を含む防錆剤が提供される。

本発明で用いられる式(I)のアシルザルコシンのアシルとしては、 n が 4 ～ 24、好ましくは n が 8 ～ 20 のものがあげられる。好ましいアシルザルコシンは、カブロイルザルコシン、カブリリルザルコシン、カブリノイルザルコシン、ミリストイルザルコシン、ペルミトイルザルコシン、ス

また、アミン付加塩を形成するのに好ましいアミンとしては、モノ、ジ又はトリアルキルアミン；シクロベンチル、シクロヘキシル又はシクロヘプチルアミン；モノ、ジ又はトリエタノールアミン、モノ、ジ又はトリプロパンノールアミンのようなアルカノールアミン；ビペラジン、ビペラジン、モルホリンのような環状アミンがあげられる。

本発明の防錆剤は、式(I)のアシルザルコシンと式(II)のベンゾトリアゾールとの混合物にアミンを付加することにより製造される。アシルザルコシンとベンゾトリアゾールとの混合には、それを容易にするために必要ならば加熱溶解手段がとられる。両混合物へのアミンの付加は、一般に 50℃ 以上、好ましくは 70 ～ 130℃ 程度に加熱することにより達成される。アシルザルコシンとベンゾトリアゾールとの混合物に付加せるアミンの量は必ずしも化学量論的である必要はない。アシルザルコシンもベンゾトリアゾールもそれ自身防錆効果があり、またアミンも防錆剤の有効性をもつ。

特開昭58-130284(3)

アシリルザルコシン、オレオイルザルコシン、ドデカノイルザルコシン等を包含する。これらは単独で又は混合物で用いることができる。しかし、アシリルザルコシンのようなヤシ油から精製されるようなものであつてよい。

式(II)のベンゾトリアゾールとしては、ベンゾトリアゾール；1-メチルベンゾトリアゾール、4-メチルベンゾトリアゾール、1-エチルベンゾトリアゾールのような低級アルキルベンゾトリアゾール；1-ヒドロキシベンゾトリアゾール、4-カルボキシベンゾトリアゾール；1-クロルベンゾトリアゾール、5-クロルベンゾトリアゾールのようなハロゲンベンゾトリアゾール；N-アセチル-、N-ブチリル-、N-ビペロイル-、N-ノナノイル-、N-カブロイル-、N-カブリリル-、N-ラウロイル-、N-ステアリル-、N-オレオイル-ベンゾトリアゾールのような N-アシリルベンゾトリアゾール等が用いられる。これらは単独で又は混合物として用いることができる。

これらの三成分は必ずしも塩の形で存在する必要はなく、ある成分が過剰に存在していてもよい。しかし、一般には 5.5 ～ 8.5 重量% の式(I)のアシルザルコシンと 4.5 ～ 1.5 重量% の式(II)のベンゾトリアゾールとの混合物 100 重量部につきアミン 4.5 ～ 8.0 重量部が付加反応せしめられる。

このようにして形成されたアミン付加塩を含む防錆剤は、実際の使用にあたつては、その有効成分の濃度が約 0.01 ～ 5 重量%、好ましくは約 0.05 ～ 2 重量% となるように希釈して用いられる。

本発明の防錆剤には、他の各種の添加剤を配合することができる。例えば、多価アルコール、多塩基性カルボン酸の部分及び全エステルやそれらのアミン誘導体、例えば、ソルビトール、ベンタエリスリトール、アルケニルこはく酸と C_6 ～ C_{11} アルコールとのエステル、 C_6 ～ C_{11} アルコールの部分又は全エステルに脂肪族、脂環式又は芳香族アミン、アルカリ金属、アルカリ土金属又はア

効果により物性を改善することができる。また、アミン付加塗の形成に用いたアミンを再度配合することもできる。また、常用されている気化性防錆剤も併用することができる。

また、本発明の防錆剤の用途によつては、潤滑性効果を要求される場合がある。本発明の防錆剤は油性剤としての効果は依然として保持しているが、さらに耐摩耗性、耐衝撃性を付与するために有機ジオキサン類金属（例えば、Zn、Pb、Sb、Cd）、アルキル又はアルケニルこはく酸のアルキルエスチル（例えばドデセニルこはく酸モノ-1-ブチル）を添加することができる。

本発明の防錆剤は、各種の分野に適用可能であり、例えばダイラー、給水タンク、ラジエーターの中に添加したり、水溶性金属加工油用、水溶性塗料、接着剤等に配合したり、或いは金属表面処理後の一次防錆等の一般の防錆剤の分野に広く用いることができる。

実施例 1

テウロイルデルコシン 30（重量%）を 6.0～

特開昭58-130284 (4)

7.0℃に加温し、ベンゾトリアゾール 1.0（重量%）を加え、完全に溶解させる。次にトリエタノールアミン 2.5（重量%）を徐々に添加し、一加し終つたならば約 110℃まで上昇させ加熱を中止し、攪拌のみを続けて放冷する。これによりアミン付加塗を含む防錆剤を得る。

このようにして得られた防錆剤を固形分が 4.5～2.0（重量%）水溶液になるよう水で適宜調整することにより防錆剤溶液を調整する。

8.0×6.0×1 mm の大きさの冷延钢板（SPCC-B）を #240 のエメリー紙で研磨し、慈ソルベントナフサ及び過メタノールでよく洗浄し、上記防錆剤溶液に電温で約 5 分間浸せきし、引き上げ室内に 2.0 時間懸垂保持したあと、JIS-Z-0236 に準拠して温潤腐食試験を 200 時間まで行なつた結果を表-1 に示す。

実施例 2～4

実施例 1 におけるようにして、表-1 に示す出発組成で各種の防錆剤を製造し、温潤腐食試験に付した。結果を表-1 に示す。

実施例 7～9

実施例 1、2 及び 5 の防錆剤に表-1 に示す該加剤を配合し、実施例 1 におけるように試験した。結果を表-1 に示す。

比較例 1 及び 2

表-1 に示す出発組成の防錆剤溶液を製造し、実施例 1 におけるように試験した。結果を表-1 に示す。

製 一

上級者用問題集

實例 10

8.0×6.0×1 mm の大きさの銅板、黄銅板及び亜鉛板を#320のエメリーペーパーで研磨し、温ソルベントナフサと温メタノール洗浄し、実施例8に示した組成液に40℃で1分間浸セキし、引き上げ室内に20時間懸垂保持したあと、JIS-Z-0256に準拠して、銅、黄銅については200時間、亜鉛については48時間腐食試験を行なった結果を表-2に示す。

二 - 二

実験例10 水溶性8の組成	比較例 アクリル酸ナトリウム トリエタノール アミン	比較例 ベンゾトリアゾール モノエタノール アミン	
耐 候 性	◎	×	△
耐 候 性		×	△
耐 候 性	○	×	×

◎；変色なし、○；わずかに変色、△；変色、

實驗例 1-1

50×25×1 mm の大きさの鋼鉄板及びアルミニウム板を 240 のエメリーペーパーで研削し、温ソルベントナフサと温メタノール洗浄し、実験例 2 に示した組成液に 50 ℃ で約 100 時間浸せきした結果を表-3 に示す。

卷 - 3

処理液 組成	実施例 10	比較例	比較例
	実施例 2 の組成	亜硝酸ナトリウム トリエタノール アミン	ベンゾトリアゾール モノエタノール アミン
対称 金属	◎	○	△
鉄 鋼	○	×	△
アルミニウム	○	×	△

◎；免耕なし、○；数点免耕、△；10~30%免耕、
×；50%以上免耕

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